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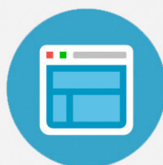
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Characteristics of copper films deposited on H_2-plasma-treated TaN substrate by chemical vapor deposition

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This work investigates the chemical vapor deposition Cu films deposited on the TaN substrate with and without an H_2-plasma treatment prior to Cu film deposition and the effect of postdeposition thermal annealing. The Cu films deposited on the H_2-plasma-treated TaN substrate have a number of favorable properties over the films deposited on the TaN substrate without the plasma treatment. These include an increased (111)-preferred orientation, smoother film surface, and a larger effective deposition rate. However, the Cu films deposited on the H_2-plasma-treated substrate have a higher electrical resistivity, presumably due to the smaller grain size. The postdeposition thermal annealing enhanced the (111)-preferred orientation and decreased the resistivity of the as-deposited Cu films. We presume that the H_2-plasma treatment, resulted in a dense and uniform distribution of hydrogen radicals adsorbed on the substrate surface, leading to the shortening of incubation time and the formation of Cu films with a smoother surface and enhanced (100)-preferred orientation. A combined process including H_2-plasma substrate treatment prior to Cu film deposition and postdeposition thermal annealing at an appropriate temperature in N_2 ambient, is proposed for the advantage of low-resistivity and high (111)-oriented Cu film deposition. © *2002 American Vacuum Society.* [DOI: 10.1116/1.1502697]

I. INTRODUCTION

The application of copper to multilevel interconnection offers a number of advantages over the conventional Al-based metallization, including lower bulk resistivity (1.67 $\mu\Omega$ cm), superior electromigration resistance, and higher resistance to stress-induced voids.[1,2] There are various techniques of copper film deposition, such as chemical vapor deposition (CVD),[3,4] conventional as well as ionized metal plasma (IMP) physical vapor deposition,[5] and electrochemical deposition (ECD) including electroplating and electroless plating;[6,7] among these, the CVD method has the advantages of superior step coverage and excellent gap filling capability for high-aspect-ratio vias and trenches,[4] making it the most promising technique of Cu film deposition for future integrated circuits (ICs) application. To implement copper into metal lines and high-aspect-ratio vias interconnection, the damascene process is developed to cope with the difficult Cu dry etching problem. Although the Cu ECD combined with IMP of a thin Cu seed layer and barrier layers provides a suitable solution for IC technologies above 0.13 μm, deposition techniques for a conformal and continuous thin barrier as well as a conformal and void-free Cu film filling into deep subquarter-micron vias, such as CVD, are eventually unavoidable for future generation devices.[8] A number of barrier materials have been used as substrates for CVD of Cu films, such as W, Ti, TiN, Ta, and TaN,[3,9–11] among these, TaN exhibits a superb barrier capability against Cu diffusion.[12] However, the chemically vapor-deposited Cu films on a TaN substrate exhibited a fairly low peak-ratio of Cu(111)/Cu(200) preferred orientation in the x-ray diffraction (XRD) spectrum,[3,11] which is unfavorable for electromigration resistance. Since the nucleation process and the microstructure of Cu films are very sensitive to the substrate surface conditions,[13,14] there have been a number of studies concerning the plasma treatment on the substrate surface prior to the Cu film deposition, resulting in the deposited Cu film with enhanced (111)-preferred orientation and superior film property.[15–17]

In this work, we investigate the effects of TaN substrate pretreatment by hydrogen (H_2) plasma on copper CVD using a multichamber low-pressure CVD system. The effects of postdeposition thermal annealing are also investigated.

II. EXPERIMENT

Figure 1 shows the schematic diagram of the multichamber Cu CVD apparatus built for this study. The apparatus consists of a cluster of four chambers and a direct liquid injection (DLI) system for precursor delivery. The chamber cluster is composed of a sample-loading chamber (for loading/unloading samples), a pretreatment chamber, a reaction chamber, and a transfer chamber. The pretreatment chamber is used to preclean and/or modify the substrate surface by plasma treatment. CVD of Cu films is to be carried out in the reaction chamber. The transfer chamber, which houses a robot arm, is designed to handle the transfer of a substrate wafer to and from each chamber. In the reaction chamber, there is a shower-head injector, through which the Cu precursor is introduced into the reaction chamber in a stream of carrier gas. Under the injector, there is a substrate susceptor that can be heated by a resistive heating element up to a maximum temperature of 400 °C. The susceptor is

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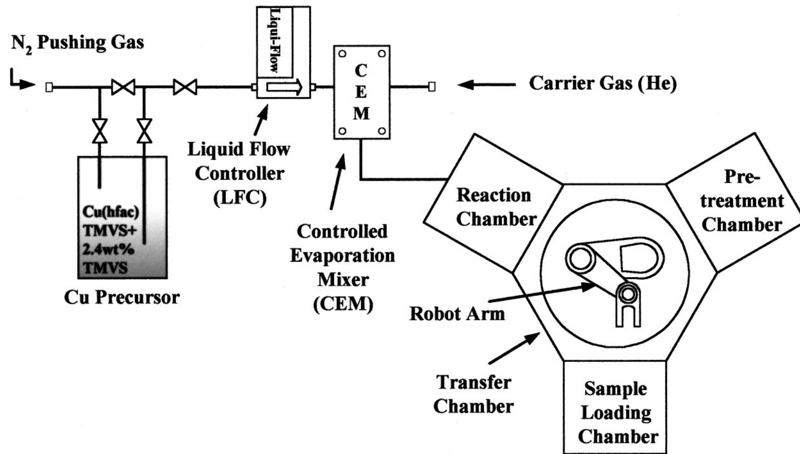

FIG. 1. Schematic diagram of multichamber Cu CVD apparatus built for this study.

also rotatable for better uniformity of film deposition. The shower-head injector is moveable in the vertical direction, so that the distance between the injector and the substrate wafer can be adjusted. The side wall of the reaction chamber and the precursor injector are kept at a temperature of 45 °C by the circulation of warm water to prevent Cu deposition of precursor condensation.

The Cu precursor used in this study is Cu(1,1,1,5,5,5-hexafluoroacetylacetonate)trimethylvinylsilane [Cu(hfac)T-MVS] with 2.4 wt % TMVS additive, which enhances the stability of the precursor.[18–20] The liquid Cu precursor is delivered by the DLI system consisting of a liquid flow controller (LFC) and a controlled evaporation mixer (CEM) (Fig. 1). Initially, the liquid precursor is propelled by N_2 gas through the LFC. It is then vaporized in the CEM and mixed with the carrier gas. Helium (He) is used as the carrier gas in this study. The precursor-saturated carrier gas is introduced into the reaction chamber through the gas injector.

In this work, TaN was used as the substrate for the CVD of Cu films. The TaN layer of 50 nm thickness was sputter deposited on a thermal-oxide (500 nm thick)-covered Si wafer. A dc magnetron sputtering system with a base pressure of 1.5×10^{-6} Torr was used to reactively sputter a Ta target (99.99% purity) in an Ar/N_2 gas mixture at a pressure of 7.6 mTorr for TaN film deposition. The flow rates of Ar and N_2 were 24 and 6 sccm, respectively, for making the gas mixture, and the TaN film was sputter deposited at a power of 150 W. The TaN-coated substrate wafer was loaded into the multichamber Cu CVD system. When the pressure of the sample-loading chamber reached 10^{-6} Torr, the substrate wafer (together with the substrate holder) was transferred to the pretreatment chamber or reaction chamber via the transfer chamber depending on the process requirement of whether the plasma pretreatment on substrate was to be performed or not. In this study, H_2 plasma treatment was performed at 50 W power for 10 min under the following conditions: H_2 flow rate 15 sccm, gas pressure 40 mTorr, substrate temperature 80 °C, and self-dc bias −259 V. After the plasma pretreatment, the substrate wafer was transferred to the reaction chamber for Cu film deposition. Prior to Cu film deposition, the substrate wafer was heated to the desired deposition temperature with He carrier gas flowing at 25 sccm and the chamber pressure maintained at 150 mTorr. Usually, approximately 1 h is required for the substrate wafer to reach the present temperature. In this study, Cu CVD was performed over a temperature range of 120 °C to 240 °C at a pressure of 150 mTorr with a precursor flow rate of 0.4 mL/min and a He carrier gas flow rate of 25 sccm. Major processing conditions and the parameters of the Cu CVD system used in this study are summarized in Table I. At the end of Cu film deposition, the substrate wafer was cooled in the ambient of He at a pressure of 150 mTorr.

The thickness of Cu films was measured using a DekTek profiler on the patterned Cu films and was verified by cross-

TABLE I. Processing conditions and parameters of the Cu CVD system.

Pretreatment chamber (H_2-plasma operating conditions)		Reaction chamber (Cu film deposition conditions)	
Substrate temperature (°C)	80	Substrate temperature (°C)	120–240
Operating pressure (mTorr)	40	Operating pressure (mTorr)	150
H_2 gas flow rate (sccm)	15	Cu precursor flow rate (mL/min)	0.4
rf power (W)	50	CEM[a] temperature (°C)	70
Self-dc bias (V)	−259	Carrier gas (He) flow rate (sccm)	25
Pretreatment time (min)	10	Substrate holder rotation speed (rpm)	10
		Gas-injector/susceptor distance (cm)	2
		Delivery line temperature (°C)	72
		Reactor wall temperature (°C)	45

[a]CEM indicates controlled evaporation mixer.

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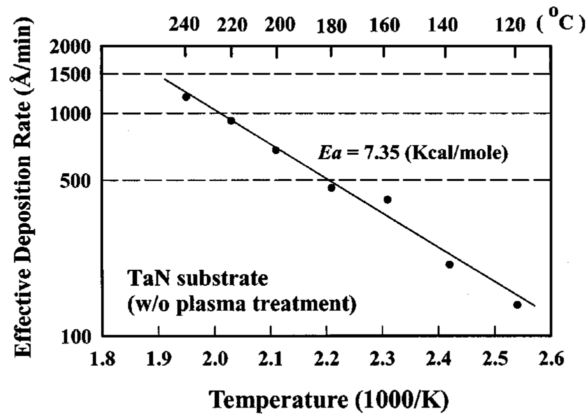


FIG. 2. Effective deposition rate vs substrate temperature (Arrhenius plot) at a constant pressure of 150 mTorr for TaN substrate.

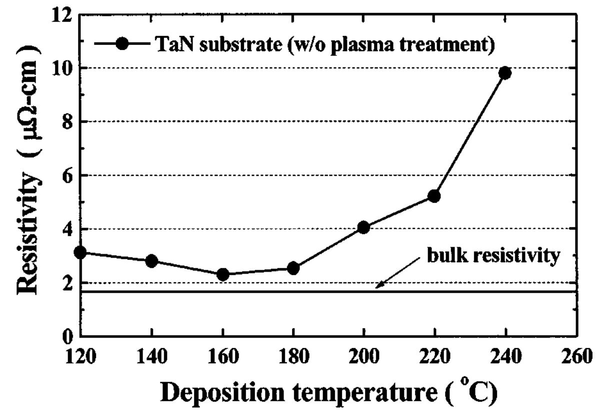


FIG. 3. Resistivity of Cu film vs deposition temperature for Cu films deposited at a constant pressure of 150 mTorr.

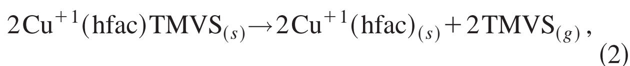
sectional scanning electron microscopy (SEM). SEM was also used to observe the surface morphology of the deposited Cu films. A four-point probe was employed to measure the sheet resistance. Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) were used to analyze the impurity content in the Cu films. The crystal structure of Cu film was identified by x-ray diffraction (XRD) analysis. The surface roughnesses of the Cu and substrate TaN films were evaluated by atomic force microscopy (AFM). Rutherford backscattering spectroscopy (RBS) was used to determine the composition of the TaN substrate layer.

III. RESULTS AND DISCUSSION

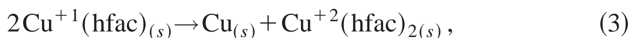
A. Chemical vapor deposition Cu films on TaN substrates without plasma pretreatment

Copper films were chemically vapor deposited on reactively sputtered TaN substrates, which have a resistivity of 0.6 mΩ cm and a composition of $TaN_{1.2}$, as determined by Rutherford backscattering. The chemical reaction of Cu CVD using Cu(hfac)TMVS as a precursor with He as a carrier gas proceeds on the substrate surface by a facile disproportionation as follows:[21,22]

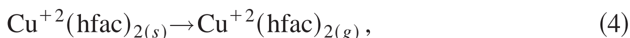
$$2Cu^{+1}(hfac)TMVS_{(g)} \rightarrow 2Cu^{+1}(hfac)TMVS_{(s)}, \quad (1)$$



$$2Cu^{+1}(hfac)TMVS_{(s)} \rightarrow 2Cu^{+1}(hfac)_{(s)} + 2TMVS_{(g)}, \quad (2)$$



$$2Cu^{+1}(hfac)_{(s)} \rightarrow Cu_{(s)} + Cu^{+2}(hfac)_{2(s)}, \quad (3)$$



$$Cu^{+2}(hfac)_{2(s)} \rightarrow Cu^{+2}(hfac)_{2(g)}, \quad (4)$$

where (g) denotes "gas phase" and (s) denotes "adsorbed on substrate surface." The reaction step 3 [Eq. (3)] is the key step of Cu nucleation on the substrate surface, which involves a process of electron exchange between the adsorbed Cu^{+1}(hfac) and the substrate surface. Thus, it is easier to deposit Cu films on the conducting substrate than the insulating substrate. Since the chemical reaction of Cu CVD involves a thermal dissociation of the Cu precursor [Eq. (2)], a higher temperature would result in a higher rate of deposition. Figure 2 shows the effective deposition rate of Cu films as a function of substrate temperature (Arrhenius plot) at a constant pressure of 150 mTorr with a He carrier gas flow rate of 25 sccm and a liquid Cu precursor flow rate of 0.4 mL/min. The effective deposition rate of Cu film was calculated using the measured thickness of a Cu film deposited for 10 min. The activation energy Ea was determined to be 7.35 kcal/mol by the Arrhenius equation

$$R = R_0 \exp(-Ea/kT), \quad (5)$$

where R is the deposition rate, R_0 is the Arrhenius pre-exponential constant or frequency factor, k is the Boltzmann constant, and T is the absolute temperature. This value of Ea is smaller than the value of 17.90 kcal/mol (deposited on TiN substrate at 0.5 Torr) reported in literature.[20] The difference in the values of the activation energy is presumably due to different deposition conditions. The resistivity of Cu films was calculated using the measured sheet resistances and films thicknesses. Figure 3 illustrates the resistivity of Cu films as a function of deposition temperature at a deposition pressure of 150 mTorr. The resistivity of CVD Cu films is closely related to the impurity content and microstructure.[23,24] The slightly higher resistivity at low deposition temperatures is presumably due to higher contamination of residual impurities from the reaction byproducts, while the high resistivity at high deposition temperatures results from the higher contamination of impurities in the film as well as the porous film structure. The optimal temperature for Cu film deposition for minimization of resistivity under the present deposition conditions appears to be around 160 °C (2.30 $\mu\Omega$ cm). Figure 4 shows SEM micrographs of the surface morphology of Cu films deposited at various temperatures for a deposition time of 10 min. The grain size of Cu increases with the deposition temperature. At higher deposition temperatures (200 °C–240 °C), the Cu films exhibit stacked grains featuring clear boundaries as well as voids between large grains. Figure 5 illustrates the Auger electron spectroscopy (AES) depth profiles of CVD Cu films deposited on TaN substrates. The most notable impurities contaminated in CVD Cu films are carbon (C) and oxygen (O), which may result from incomplete desorption of hfac ligand during the CVD process.[24] Although fluorine (F)

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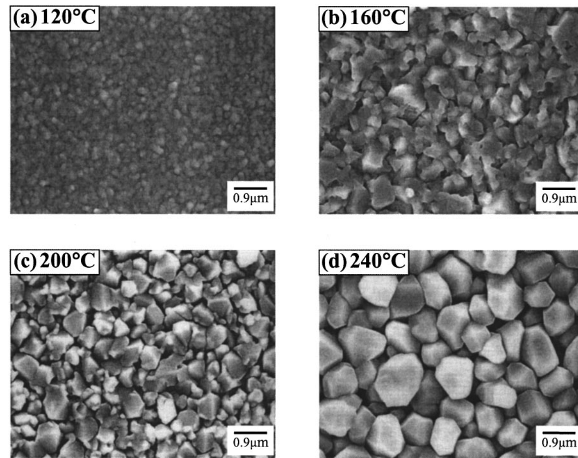

FIG. 4. SEM micrographs showing surface morphology of Cu films deposited on TaN substrates at a temperature of (a) 120 °C, (b) 160 °C, (c) 200 °C, and (d) 240 °C. The films were deposited at a constant pressure of 150 mTorr for 10 min (without plasma treatment prior to Cu deposition).

impurity was not detected in the AES depth profile, the SIMS analysis shown in Fig. 6 reveals obvious F contamination in Cu film.

B. Nucleation and surface morphology observation

The nucleation process and the microstructure of Cu films are very sensitive to the substrate surface conditions, which play an important role in the CVD of Cu films. Figure 7 shows atomic force microscopy (AFM) images of the TaN substrate before and after H_2-plasma treatment at 50 W for 10 min. The H_2-plasma treatment slightly improved the surface smoothness of the TaN substrate. In order to study the effect of substrate pretreatment by H_2 plasma, the nucleation process of Cu films was investigated. Figure 8 shows SEM micrographs for the nucleation process of Cu films deposited at 160 °C on a TaN substrate with and without a H_2-plasma treatment. On the TaN substrate without H_2-plasma treatment, the Cu-containing adspecies were sparsely nucleated on the substrate surface, and the subsequent adspecies tend to nucleate on the existing Cu nuclei rather than the TaN substrate. As a result, the Cu nuclei grew into Cu grains sparsely distributed on the substrate, while a few new Cu nuclei may also randomly nucleated directly on the TaN substrate, forming smaller Cu grains [Fig. 8(a)]. After 2 min deposition, all grains grew larger, though a few smaller new grains are scat-

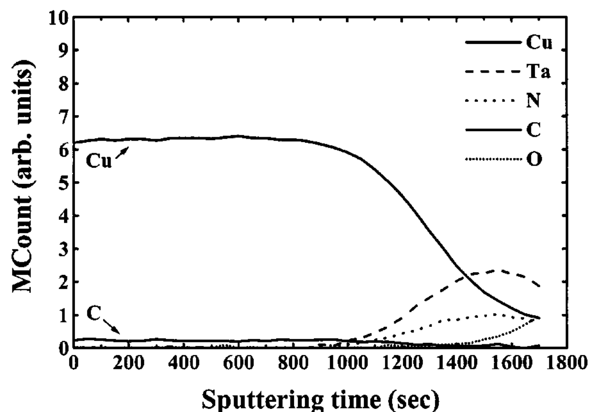

FIG. 5. AES depth profiles of Cu films deposited on TaN substrate at 160 °C for 10 min (without plasma treatment prior to Cu deposition).

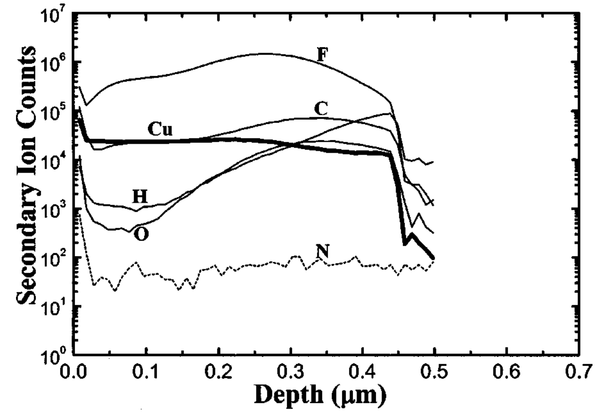

FIG. 6. SIMS depth profiles of Cu films deposited on TaN substrate at 160 °C for 10 min (without plasma treatment prior to Cu deposition).

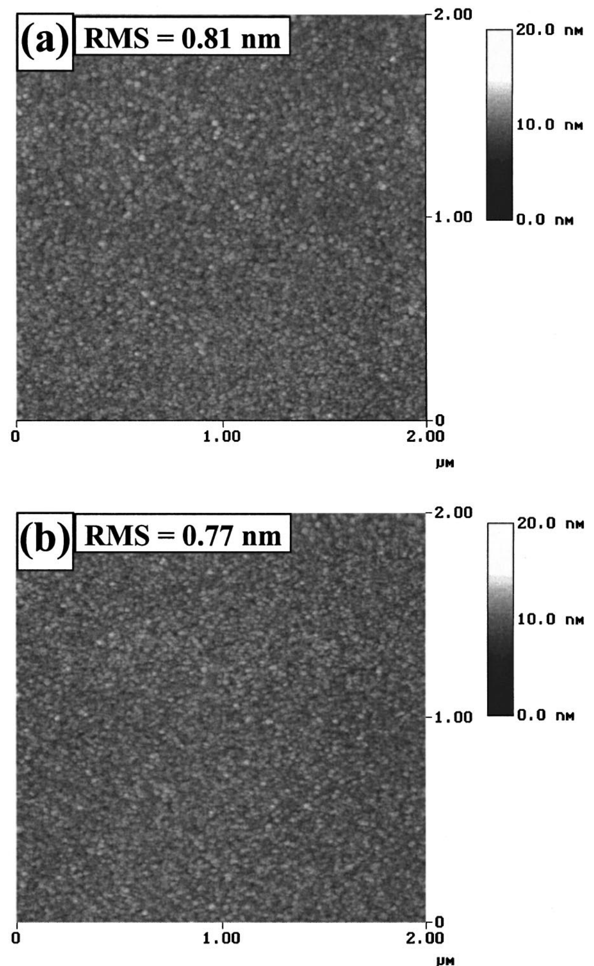

FIG. 7. AFM images showing surface morphology of TaN substrates (a) without plasma treatment, and (b) with H_2-plasma treatment at 50 W (with 40 mTorr pressure for a plasma time of 10 min).

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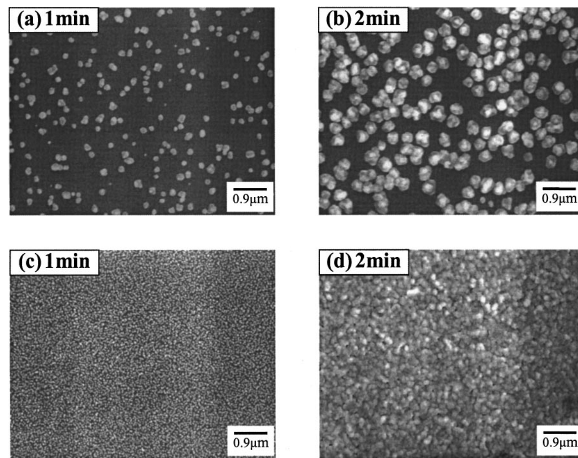

FIG. 8. SEM micrographs showing Cu nucleation at 160 °C for (a) 1 min and (b) 2 min deposition on TaN substrate without plasma treatment, and (c) 1 min and (d) 2 min deposition on TaN substrate with H_2-plasma treatment.

tered among the larger ones [Fig. 8(b)]. On the H_2-plasma-treated TaN substrate, the Cu-containing adspecies [Cu(hfac)] was easily and uniformly nucleated on the substrate surface, forming dense and small Cu nuclei after 1 min deposition [Fig. 8(c)]. The Cu-containing adspecies continuously adsorbed on the surface of the Cu nuclei to proceed with the growth of copper nuclei, resulting in larger Cu grains and a continuous Cu film after 2 min deposition [Fig. 8(d)]. A similar result was reported in literature that the nucleation of Cu on the H_2-plasma-treated TiN substrate led to a dense distribution of Cu grains.[25] The nucleation of Cu on the TaN substrate is closely related to the substrate surface conditions. On the H_2-plasma-treated TaN substrate surface, there are many uniformly adsorbed hydrogen radicals and/or atoms.[25,26] This surface hydrogen may enhance the chemisorption of Cu-containing adspecies [Cu(hfac)] on the substrate surface through the direct bonding between the surface hydrogen and the CH radical in the Cu precursor.[26] Thus, Cu can be easily and uniformly nucleated on the H_2-plasma-treated TaN substrate surface, resulting in shortened incubation time and densely distributed Cu grains. The dense and uniform distribution of Cu grains on the H_2-plasma-treated TaN substrate indicates that the substrate has a higher surface energy or lower interfacial energy, leading to nucleation of Cu with a smaller wetting angle (contact angle).[16,27,28] The smaller wetting angle would enhance the growth of Cu film in two dimensions (layer growth), forming the most stable and (111) closely packed configuration.[16] The SEM micrograph in Fig. 9 shows the surface morphology of a Cu film deposited at 160 °C for 10 min on the H_2-plasma-treated TaN substrate. In comparison with the corresponding Cu film deposited on the TaN substrate without H_2-plasma treatment [Fig. 4(b)], the surface morphology of the Cu film deposited on the H_2-plasma-treated TaN substrate is characterized by regularly shaped smaller grains. As a result, superior surface smoothness is expected for the Cu film deposited on the H_2-plasma-treated TaN substrate. This is indicated by the results of AFM analysis shown in Fig. 10.

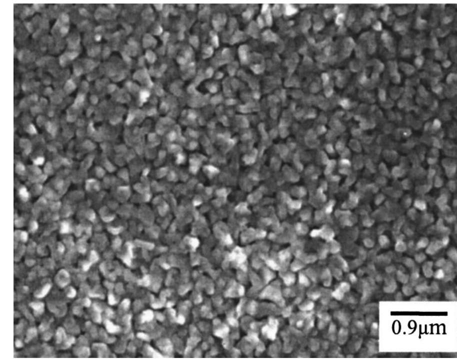

FIG. 9. SEM micrograph showing surface morphology of Cu film deposited at 160 °C and 150 mTorr for 10 min on H_2-plasma-treated TaN substrate.

The Cu film deposited on the TaN substrate without H_2-plasma treatment shows irregular Cu grains with an average surface roughness root-mean square (rms) of 56 nm, while the Cu film deposited on the H_2-plasma-treated TaN substrate shows regularly shaped smaller grains with an average surface roughness (rms) of 20 nm.

The thicknesses of the Cu films deposited on the TaN substrate with and without an H_2 plasma treatment were measured to be 509 and 408 nm, respectively, for a 10 min deposition at a substrate temperature of 160 °C. The thicker Cu film on the H_2-plasma-treated TaN substrate is presumably due to the shorter incubation time and the much denser Cu nuclei during the nucleation stage. The resistivity of the Cu film deposited on the H_2-plasma-treated TaN substrate was determined to be 2.82 $\mu\Omega$ cm, which is higher than that of the Cu film deposited on the substrate without the plasma

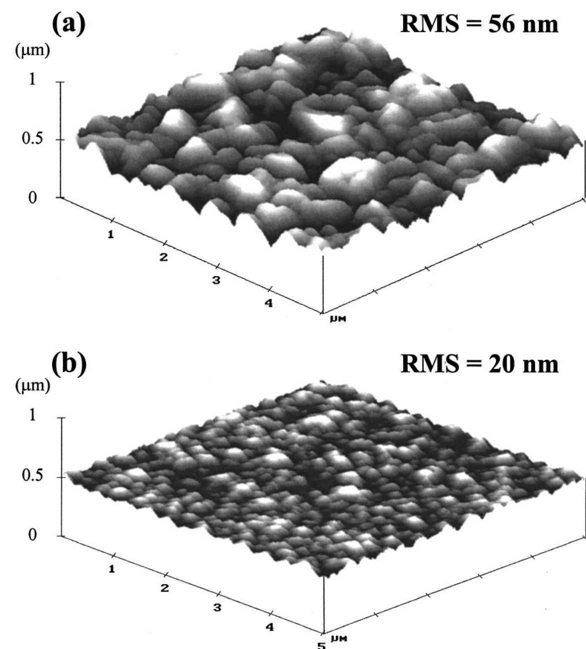

FIG. 10. AFM images showing surface morphology of Cu films deposited on TaN substrates (a) without plasma treatment and (b) with H_2-plasma treatment prior to Cu deposition.

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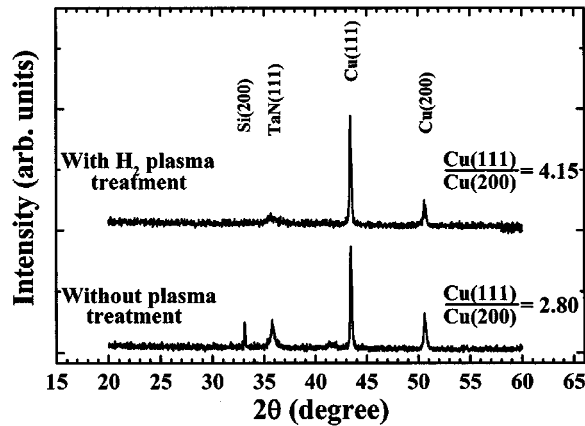

FIG. 11. XRD spectra of Cu films deposited on TaN substrates with and without H_2-plasma treatment prior to Cu deposition.

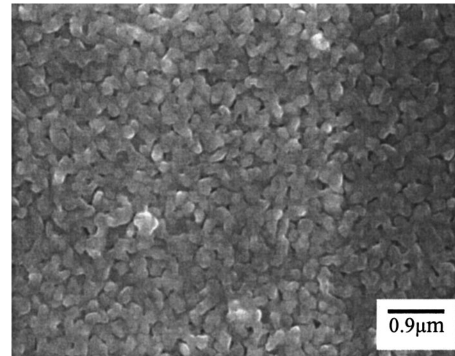

FIG. 12. SEM micrograph showing surface morphology of Cu film deposited on H_2-plasma-treated TaN substrate followed by thermal annealing at 400 °C for 30 min in N_2 ambient.

treatment (2.30 $\mu\Omega$ cm), presumably due to the smaller Cu grains and thus a higher boundary density.

C. Preferred orientation and postdeposition thermal annealing

The H_2-plasma treatment on the TaN substrate also affects the preferred orientation of deposited Cu films. Figure 11 shows the XRD spectra for Cu films deposited on TaN substrates with and without an H_2-plasma treatment. It can be seen that the peak ratio of Cu(111) to Cu(200) reflection increased from 2.80 to 4.15 resulting from the H_2-plasma treatment on the TaN substrate. With the H_2-plasma treatment, there are many uniformly adsorbed hydrogen radicals on the TaN substrate surface, which enable the chemisorption of Cu-containing adspecies on the substrate surface, leading to the formation of Cu film with enhanced (111)-preferred orientation because the (111) texture is the most stable configuration.[16,28]

Copper films deposited on the TaN substrate were thermally annealed at 400 °C for 30 min in an N_2 ambient. Figure 12 shows the surface morphology of the thermally annealed Cu film deposited on the H_2-plasma-treated TaN substrate. In comparison with the as-deposited Cu film (Fig. 9), the thermally annealed Cu film reveals a closer contact between Cu grains, similar to those reported in literature for CVD Cu films annealed in Ar and Ar/H_2 ambients.[29] Moreover, thermal annealing also resulted in a decrease in film resistivity as well as an increase in the peak ratio of Cu(111) to Cu(200) reflection, as shown in Table II. The decrease in film resistivity is presumably due to the closer contact between the Cu grains. In addition, we presume that the Cu film deposited on the H_2-plasma-treated substrate possesses a uniform surface energy and little variation of film stress because of the better regular arrangement of Cu grains. Thermal annealing would reduce the grain boundary and surface energy of the Cu film, resulting in the recrystallization of Cu grains to forming the most stable (111) texture.[16,30] On the other hand, Cu grains of different sizes are irregularly arranged for the Cu film deposited on the TaN substrate without a plasma treatment; thus, there are nonuniform surface energy and nonuniform films stress, and this nonuniformity would be reduced in order to reduce the total system energy during thermal annealing.[30] As a result, there is not enough driving force to recrystallize the Cu grains for the formation of the most stable (111) texture, and the improvement of the Cu(111)/Cu(200) reflection peak ratio was relatively moderate as compared with the Cu film deposited on the H_2-plasma-treated substrate. A similar observation was also reported for CVD Cu films thermally annealed at 450 °C in Ar and Ar/H_2 ambients.[29] With regard to adhesion of Cu films, a Scotch tape pulling test was used to qualify the adhesion between the CVD Cu films and the TaN substrate. All samples with the Cu film deposited at 160 °C and 150 mTorr, irrespective of substrate pretreatment by H_2-plasma and/or postthermal annealing, passed the Scotch tape test. In summary, we conclude that the TaN substrate surface with uniform and dense hydrogen adatom resulting from the H_2-plasma treatment, is responsible for the improvement of various Cu film properties.

TABLE II. Effects of thermal annealing (400 °C/30 min) on Cu film resistivity and peak ratio of Cu(111)/Cu(200) reflection.

H_2-plasma treatment on TaN substrate	Film resistivity ($\mu\Omega$ cm)		Cu(111)/Cu(200) peak ratio	
	As deposited	After annealing	As deposited	After annealing
No	2.30	2.15	2.80	3.10
Yes	2.82	2.25	4.15	5.52

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IV. CONCLUSION

This work investigates the CVD Cu films deposited on the TaN substrate with and without an H_2-plasma treatment and the effect of postdeposition thermal annealing. The Cu films deposited on the H_2-plasma-treated TaN substrate have a number of favorable properties over the films deposited on the TaN substrate without the plasma treatment. These include an increased (111)-preferred orientation, smoother film surface, and a larger effective deposition rate. However, the Cu films deposited on the H_2-plasma-treated substrate have a higher electrical resistivity, presumably due to the smaller grain size, and thus higher grain-boundary density. Postdeposition thermal annealing resulted in the reduction of electrical resistivity and the increase of Cu(111)/Cu(200) reflection ratio. We presume that the H_2-plasma treatment resulted in a dense and uniform distribution of hydrogen radicals (and/or atoms) adsorbed on the substrate surface, leading to the shortening of incubation time and the formation of Cu films with a smoother surface and enhanced (111)-preferred orientation. A combined process including H_2 plasma substrate treatment prior to Cu film deposition and postdeposition thermal annealing at an appropriate temperature (e.g., 400 °C) in an N_2 ambient, is proposed for the advantage of low-resistivity and high (111)-oriented Cu film deposition. In this way, Cu film with a resistivity of 2.25 $\mu\Omega$ cm and a Cu(111)/Cu(200) peak ratio of 5.52 was obtained.

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